

WE CLAIM:

1. A process comprising:

continuously contacting, in a distillation column reactor comprising a reaction zone and a distillation zone, benzene with a zeolite catalyst effective to hydroxylate benzene and an oxidant at a temperature in the range of from above 100°C to 270°C thereby producing a hydroxylated product, wherein at least a portion of said benzene being in a liquid phase;

continuously separating said hydroxylated product from the un-reacted benzene in the distillation zone under conditions effective to vaporize said un-reacted benzene and maintain said hydroxylated product in a liquid phase; and
recovering the said hydroxylated product from the distillation column reactor.

2. The process of claim 1 wherein said separating comprises fractional distillation.

3. The process of claim 1 wherein the oxidant is selected from the group consisting of nitrous oxide, oxygen, air, and mixtures thereof.

4. The process of claim 2 wherein the oxidant is selected from the group consisting of nitrous oxide, oxygen, air, and mixtures thereof.

5. The process of claim 1 wherein the oxidant is nitrous oxide.

6. The process of claim 2 wherein the oxidant is nitrous oxide.

7. The process of claim 1 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

8. The process of claim 2 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

9. The process of claim 3 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

10. The process of claim 3 wherein selectivity for conversion of said oxidant to hydroxylated product is at least 90 mol %.

11. The process of claim 3 wherein selectivity for conversion of said oxidant to hydroxylated product is at least 95 mol %.

12. The process of claim 1 wherein said zeolite catalyst is a zeolite comprising at least one metal selected from the group consisting of ruthenium, rhodium, iridium, iron, magnesium, cobalt, copper, titanium, vanadium, manganese, niobium, and mixtures thereof.

13. The process of claim 2 wherein said zeolite catalyst is a zeolite comprising at least one metal selected from the group consisting of ruthenium, rhodium, iridium, iron, magnesium, cobalt, copper, titanium, vanadium, manganese, niobium, and mixtures thereof.

14. The process of claim 3 wherein said zeolite catalyst is a zeolite comprising at least one metal selected from the group consisting of ruthenium, rhodium, iridium, iron, magnesium, cobalt, copper, titanium, vanadium, manganese, niobium, and mixtures thereof.

15. The process of claim 7 wherein said zeolite catalyst is a zeolite comprising at least one metal selected from the group consisting of ruthenium, rhodium, iridium, iron, magnesium, cobalt, copper, titanium, vanadium, manganese, niobium, and mixtures thereof.

16. The process of claim 7 wherein said zeolite catalyst comprises the metal in an amount of about 0.01 wt % to about 5 wt%.

17. The process of claim 8 wherein said zeolite catalyst comprises metal in an amount of from about 0.01 wt % to about 5 wt%.

18. The process of claim 9 wherein said zeolite catalyst comprises metal in an amount from about 0.01 wt % to about 5 wt%.

19. The process of claim 10 wherein said zeolite catalyst comprises metal in an amount from about 0.01 wt % iron to about 5 wt% iron.

20. The process of claim 5 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

21. The process of claim 10 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

22. The process of claim 12 wherein said conditions comprise a temperature of from about 185 °C. to about 270 °C.

23. The process of claim 1 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm.

24. The process of claim 2 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm .

25. The process of claim 3 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm.

26. The process of claim 5 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm .

27. The process of claim 7 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm.

28. The process of claim 12 wherein said conditions comprise a benzene partial pressure in the range of from about 0.1 atm to about 45 atm.

29. The process of claim 1 further comprising withdrawing said un-reacted benzene and oxidant as overhead.

30. A process comprising

continuously contacting, in a distillation column reactor comprising a reaction zone and a distillation zone, benzene with an oxidant in a distillation column reactor at a temperature in the range of from above 100°C to 270°C and a benzene partial pressure in the range of from about 0.1 atm to about 45 atm to form phenol wherein at least a portion of said benzene being in a liquid phase, said distillation column reactor comprising a zeolite catalyst effective to hydroxylate said benzene; and

continuously separating said phenol from the un-reacted benzene in the distillation zone under conditions effective to vaporise said un-reacted benzene and maintain said phenol in a liquid phase; and

recovering the said phenol from the distillation column reactor.

31. The process of claim 30 wherein the oxidant comprises nitrous oxide. .

32. The process of claim 31 wherein said separation comprises fractional distillation. 33. The process of claim 30 further comprising withdrawing said vaporized un-reacted benzene and oxidant as overhead.

34. The process of claim 30 wherein the temperature of the distillation zone is higher than the boiling point of benzene and lower than the boiling point of phenol.

35. The process of claim 31 wherein selectivity for conversion of nitrous oxide to phenol is at least about 90 mol %.

36. The process of claim 30 wherein said zeolite catalyst comprises a zeolite comprising from about 0.01 wt % of at least one metal to about 5 wt% of at least one metal selected from the group consisting of ruthenium, rhodium, iridium, titanium, magnesium, cobalt, copper, vanadium, manganese, niobium, and iron.

37. The process of claim 34 wherein said zeolite catalyst comprises a zeolite comprising from about 0.01 wt % of at least one metal to about 5 wt% of at least one metal selected from the group consisting of ruthenium, rhodium, iridium, titanium, magnesium, cobalt, copper, vanadium, manganese, niobium, and iron.

38. ³⁷ A process for catalytic hydroxylation of benzene comprising:

continuously contacting, in a distillation column reactor comprising a reaction zone and a distillation zone, benzene with an oxidant in a distillation column reactor at a temperature in the range of from above 100°C to 270°C and a benzene partial pressure in the range of from about 0.1 atm to about 45 atm to form phenol wherein at least a portion of said benzene being in a liquid phase, said distillation column reactor comprising a zeolite catalyst effective to hydroxylate said benzene; and

continuously separating said phenol from the unreacted benzene in the distillation zone by fractional distillation; and

recovering the said phenol from the distillation column reactor.

39. The process of claim 38 wherein the temperature of the distillation zone is higher than the boiling point of benzene and lower than the boiling point of phenol .

40. The process of claim 38 wherein said oxidant comprises nitrous oxide.

41. The process of claim 38 wherein said zeolite catalyst contains from about 0.1 wt. % iron to about 1.0 wt. % iron.

42. The process of claim 36 wherein said zeolite catalyst comprises iron.

43. The process of claim 42 wherein the zeolite is an alumino-silicate that does not contain additional boron content.

44. The process of claim 42 further comprising withdrawing said vaporized un-reacted benzene and oxidant as overhead.

45. The process of claim 16 wherein the zeolite is an alumino-silicate that does not contain additional boron content.

46. The process of claim 1 wherein the zeolite catalyst comprises at least one zeolite selected from the group consisting of zeolite of the structural types MFI, MEL, FER, FAU, BEA ,MFS, NES, MOR,, MTT, MWW, EUO, OFF, MTW

and zeolites ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, SSZ-39, and PSH-3 and mixtures thereof.

47. The process of claim 46 wherein the hydroxylated product comprises phenol.

48. The process of claim 1 wherein the hydroxylated product comprises phenol.

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~~49.~~ The process of claim 30 wherein the zeolite catalyst comprises at least one zeolite selected from the group consisting of zeolite of the structural types MFI, MEL, FER, FAU, BEA, MFS, NES, MOR, MTT, MWW, EUO, OFF, MTW and zeolites ITQ-1, ITQ-2, MCM-56, MCM-49, ZSM-48, SSZ-35, SSZ-39, and PSH-3 and mixtures thereof.